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Theory of the dynamic magnetic susceptibility of ferrofluids

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The dynamic magnetic response of a ferrofluid to a weak ac magnetic field is studied using new statistical mechanical theory and Brownian dynamics simulations, taking account of dipole-dipole interactions between the constituent ferromagnetic colloidal particles, and the presence of a range of particle sizes. The effects of interactions and polydispersity on the frequency dispersion are shown to be substantial: the amplitude of the response can be about twice that of a noninteracting system; the frequency for peak power loss can be reduced by about one half; and polydispersity effects can even change the qualitative appearance of the susceptibility spectrum.

Ferrofluids are colloidal suspensions of ferromagnetic, single-domain nanoparticles in a nonmagnetic carrier liquid [1]. They are functional materials with many physical properties that can be switched by the application of external magnetic fields or field gradients. One of the most important properties of a ferrofluid is its initial magnetic susceptibility $\chi = (\partial M / \partial H)_{H=0}$, describing the response of the magnetization M to a weak magnetic field H . The statistical-mechanical link between the microscopic and bulk properties of magnetic materials has been a major topic of interest since the seminal works by Langevin on noninteracting systems [2], and Weiss on mean-field theory [3], in the early 20th Century. Many theories have been developed alongside experimental measurements on ferrofluids, in order to understand how the interparticle dipole-dipole interactions, and resulting orientational correlations, control the magnetic response. Of particular importance is how the particle-size distribution affects the material properties. Ferrofluids are often highly polydisperse, and the particle dipole moment scales with the particle volume. It is challenging to account for the strong correlations between large particles; at low concentrations, self-assembled structures such as rings may reduce the susceptibility [4], while at high concentrations, the dipolar correlations have the opposite effect [5].

The *dynamic* magnetic susceptibility $\chi(\omega)$ describes the response of M to an ac magnetic field with angular frequency ω . The power loss is proportional to the square of the imaginary (out-of-phase) part $[\chi''(\omega)]^2$ [6], which possesses a peak at a characteristic frequency ω_0 . The resulting dissipation of heat is used in medical therapies such as localized hyperthermia of diseased tissue [7]. Debye theory gives expressions for $\chi(\omega)$ in the case of noninteracting systems [8], but taking account of strong particle interactions and polydispersity is an open problem.

In this Rapid Communication, the effects of interactions and polydispersity on the dynamic susceptibility are examined using a modified mean-field (MMF) theory [9]

and a new ‘modified Weiss’ (MW) theory. The theoretical predictions are tested rigorously against new results from Brownian dynamics (BD) simulations. It is shown that the effects of particle interactions and polydispersity are very strong, in terms of both the static susceptibility $\chi = \chi(0)$, and the frequency dispersion $\chi(\omega)$. Therefore, such effects must be taken into account when interpreting experimental measurements on real ferrofluid samples, and the MW theory provides an accurate means of doing so.

The ferrofluid is modeled as a suspension of N spherical ferromagnetic nanoparticles in a long cylinder of volume V , with the long axis aligned with the laboratory z axis (to eliminate demagnetization fields). The diameter of the uniformly magnetized core of a particle is x , and the magnitude of the dipole moment is $\mu(x) = \pi x^3 M_s / 6$, where M_s is the saturation magnetization of the ferromagnetic material; the dipole moment vector of particle 1 in spherical polar coordinates is $\boldsymbol{\mu}_1 = \mu_1(\sin \theta_1 \cos \phi_1, \sin \theta_1 \sin \phi_1, \cos \theta_1)$ where $\mu_1 = \mu(x_1)$. The normalized particle-size probability distribution function is $p(x)$. A weak, linearly polarized, ac magnetic field $\mathbf{h} = (0, 0, h e^{-i\omega t})$ is applied parallel to the z direction, where h is the amplitude and t is the time. The dipole-field interaction energy of particle 1 is $U_1^h = -\mu_0 \boldsymbol{\mu}_1 \cdot \mathbf{h}$, and the dipole-dipole interaction energy between particles 1 and 2 is

$$U_{12}^d = \frac{\mu_0}{4\pi} \left[\frac{(\boldsymbol{\mu}_1 \cdot \boldsymbol{\mu}_2)}{r_{12}^3} - \frac{3(\boldsymbol{\mu}_1 \cdot \mathbf{r}_{12})(\boldsymbol{\mu}_2 \cdot \mathbf{r}_{12})}{r_{12}^5} \right] \quad (1)$$

where μ_0 is the vacuum permeability, \mathbf{r}_{12} is the center-center separation vector, and $r_{12} = |\mathbf{r}_{12}|$. The bulk magnetization along the z direction is

$$M(t) = n \langle \mu_1 \cos \theta_1 W_1 \rangle_1 \quad (2)$$

where $n = N/V$ is the concentration of particles, $W_1 = W(\theta_1, t)$ is the time-dependent orientational distribution function (ODF) for particle 1, and $\langle \dots \rangle_1 =$

$(4\pi)^{-1} \int_0^\infty p(x_1) dx_1 \int_{-1}^1 d \cos \theta_1 \int_0^{2\pi} d\phi_1 \dots$ is an average over both the size and the orientation of the particle. W_1 is governed by the Fokker-Planck-Brown (FPB) equation [9–11]

$$2\tau_1 \frac{\partial W_1}{\partial t} = \frac{1}{\sin \theta_1} \frac{\partial}{\partial \theta_1} \left[\sin \theta_1 \left(\frac{\partial W_1}{\partial \theta_1} + \frac{W_1}{k_B T} \frac{\partial U_1^h}{\partial \theta_1} + \frac{n}{k_B T} \int \left\langle g_{12} \frac{\partial U_{12}^d}{\partial \theta_1} \right\rangle_2 d\mathbf{r}_2 \right) \right] \quad (3)$$

where $\tau_1 = \tau(x_1)$ is the characteristic Brownian rotation time for particle 1, k_B is Boltzmann's constant, and g_{12} is the pair correlation function (PCF) between particles 1 and 2 [12]. For particles with hydrodynamic diameter $\sigma \geq x$ in a solvent with viscosity η , $\tau = \pi\eta\sigma^3/2k_B T$. At equilibrium, the quantity $(\dots) = 0$ and is equivalent to the Yvon-Born-Green equation linking the one-particle and two-particle distribution functions [12]. This is assumed to carry over to the time-dependent case, on the basis that the ac field is weak, and hence the response of the ODF is linear and small. The last term in (3) represents a weighted mean of the magnetic field experienced by particle 1 due to all of the other particles. Inertial effects and Néel rotation (superparamagnetism) are omitted from (3) for simplicity. Including inertia would only affect the short-time dynamics, and would not interfere with the overdamped, Brownian dynamics which characterizes real colloidal particles. The Néel mechanism decreases the timescale for the magnetic response, but it is not strongly affected by interactions.

The time-dependent ODF can be determined in weak ac fields by writing $W_1 = 1 + \alpha_1 \cos \theta_1 A_1 e^{-i\omega t}$ where $\alpha_1 = \mu_0 \mu_1 h / k_B T$ is the Langevin parameter, and $A_1 = A(\omega, x_1)$ is a coefficient to be determined. The magnetization is given by (2), and the corresponding susceptibility spectrum is $\chi(\omega) = \partial M(t) / \partial (h e^{-i\omega t})$.

$$\chi(\omega) = \frac{\mu_0 n}{3k_B T} \int p(x_1) \mu_1^2 A_1 dx_1 \quad (4)$$

The solutions of the FPB equation in various cases are outlined below [13].

Debye theory In the case of noninteracting particles ($n \rightarrow 0$), solving (3) gives $A_1^D = (1 - i\omega\tau_1)^{-1}$ (D means Debye). Dropping the subscript 1, the real and imaginary parts of $\chi_D(\omega) = \chi'_D(\omega) + i\chi''_D(\omega)$ are then

$$\begin{aligned} \chi'_D(\omega) &= \frac{\mu_0 n}{3k_B T} \int_0^\infty p(x) \left[\frac{\mu^2(x)}{1 + \omega^2 \tau^2(x)} \right] dx \\ \chi''_D(\omega) &= \frac{\mu_0 n}{3k_B T} \int_0^\infty p(x) \left[\frac{\mu^2(x) \omega \tau(x)}{1 + \omega^2 \tau^2(x)} \right] dx. \end{aligned} \quad (5)$$

The Langevin static susceptibility is $\chi_L = \chi_D(0) = (\mu_0 n / 3k_B T) \int_0^\infty p(x) \mu^2(x) dx$.

MMF theory The leading-order correction to the Debye theory can be obtained by writing the PCF as $g_{12} = W_1 W_2^D \Theta_{12} + O(n)$, where W_2^D is the Debye-theory ODF for particle 2, and $\Theta_{12} = \Theta(r_{12} - \sigma_{12})$ is the Heaviside function representing the impenetrability of two particles

with average hard-sphere diameter σ_{12} . The interaction energy of particle 1 is given by

$$\int \langle W_2^D U_{12}^d \Theta_{12} \rangle_2 d\mathbf{r}_2 = -\frac{\mu_0 \alpha_1 \cos \theta_1 e^{-i\omega t}}{9} \int_0^\infty p(x_2) \mu_2^2 A_2^D dx_2 \quad (6)$$

where the integral over \mathbf{r}_2 depends on the shape of the sample. Including this interaction term in the FPB equation (3) yields the coefficient

$$A_1^{\text{MMF}} = \frac{1}{1 - i\omega\tau_1} \left[1 + \frac{1}{3} \chi_D(\omega) \right] \quad (7)$$

where $\chi_D(\omega)$ appears because it is related to the integral over x_2 in (6) through (4). Putting this in to (4) gives $\chi_{\text{MMF}}(\omega) = \chi_D(\omega) [1 + \chi_D(\omega)/3]$, expressed entirely in terms of the Debye functions.

$$\begin{aligned} \chi'_{\text{MMF}}(\omega) &= \chi'_D(\omega) + \frac{1}{3} \left\{ [\chi'_D(\omega)]^2 - [\chi''_D(\omega)]^2 \right\} \\ \chi''_{\text{MMF}}(\omega) &= \chi''_D(\omega) \left[1 + \frac{2}{3} \chi'_D(\omega) \right] \end{aligned} \quad (8)$$

The static susceptibility is $\chi_{\text{MMF}}(0) = \chi_L(1 + \chi_L/3)$, which is exact to order χ_L^2 [14]. The dynamical MMF expressions have been tested against results from BD simulations of monodisperse particles, and they are only accurate if $\chi_L \lesssim 1$ [15]. It is shown below how they fail for ferrofluids at high concentration and/or low temperature.

MW theory Weiss' mean-field theory is based on a self-consistent determination of the ODF. In this case, the PCF is written $g_{12} = W_1 W_2 \Theta_{12}$. Following exactly the same route as MMF theory yields the coefficient

$$A_1^W = \frac{1}{1 - i\omega\tau_1} \left[1 + \frac{1}{3} \chi(\omega) \right] \quad (9)$$

where $\chi(\omega)$ is itself the function to be determined. Inserting this coefficient in to (4) gives the expression

$$\chi_W(\omega) = \frac{\chi_D(\omega)}{1 - \frac{1}{3} \chi_D(\omega)}. \quad (10)$$

In the static limit $\chi_W(0) = \chi_L / (1 - \chi_L/3)$, which predicts a divergence at $\chi_L = 3$ associated with a transition to a long-range ordered ferromagnetic state. This transition has not been observed in any magnetic liquid. To obtain the correct expression for $\chi(0)$ to order χ_L^2 , the numerator and denominator of (10) are multiplied by $(1 + \chi_L/3)$, and the term of order $\chi_L \chi_D$ responsible for the divergence is omitted, yielding a new MW expression

$$\chi_{\text{MW}}(\omega) = \frac{(1 + \frac{1}{3} \chi_L) \chi_D(\omega)}{1 + \frac{1}{3} \chi_L - \frac{1}{3} \chi_D(\omega)}. \quad (11)$$

This now gives the correct static susceptibility without a divergence. The real and imaginary parts of this function are

$$\begin{aligned} \frac{\chi'_{\text{MW}}(\omega)}{(1 + \frac{1}{3} \chi_L)} &= \frac{(1 + \frac{1}{3} \chi_L) \chi'_D(\omega) - \frac{1}{3} \left\{ [\chi'_D(\omega)]^2 + [\chi''_D(\omega)]^2 \right\}}{[1 + \frac{1}{3} \chi_L - \frac{1}{3} \chi'_D(\omega)]^2 + \frac{1}{9} [\chi''_D(\omega)]^2} \\ \frac{\chi''_{\text{MW}}(\omega)}{(1 + \frac{1}{3} \chi_L)} &= \frac{(1 + \frac{1}{3} \chi_L) \chi''_D(\omega)}{[1 + \frac{1}{3} \chi_L - \frac{1}{3} \chi'_D(\omega)]^2 + \frac{1}{9} [\chi''_D(\omega)]^2}. \end{aligned} \quad (12)$$

The focus here is on the effects of interactions and polydispersity on the magnetic response. The three theories are therefore tested against BD simulations, which are like ideal computational experiments in which inertial effects and the Néel mechanism are suppressed, and the particle-size distribution is strictly controlled, hence isolating the effects of interest. The first test is against existing BD simulation results for monodisperse ferrofluids with dipolar coupling constant $\lambda = \mu_0 \mu^2 / 4\pi \sigma^3 k_B T = 1$, where σ is the particle diameter in the Weeks-Chandler-Andersen soft-sphere potential [15]. The volume fraction is $0.0 \leq \varphi = \pi n \sigma^3 / 6 \leq 0.367$, and the Langevin susceptibility is $\chi_L = 8\varphi\lambda$. Figure 1(a) shows $\chi(\omega)$ from the Debye, MMF, and MW theories, and BD simulations, for the case $\varphi = 0.314$ and $\chi_L = 2.51$. Debye theory is completely inadequate, MMF and MW theories give the same static susceptibility, but MW theory is superior in terms of the frequency dispersion. Figure 1(b) shows ω_0 as a function of χ_L . MW theory correctly predicts the dependence over the whole range of χ_L , while MMF theory gets only the low- χ_L dependence correct. The decrease in peak frequency by about one half is due to the orientational correlations between particles, and the resulting increase in characteristic rotational time. Figure 1(c) and (d) shows the quantities a and b defined by the low-frequency behavior of $\chi(\omega)$: $\chi'(\omega) = \chi(0)[1 - a(\omega\tau)^2]$; $\chi''(\omega) = b\chi_L\omega\tau$; both are defined such that in the noninteracting case, $a = b = 1$. Again, MW theory is superior to MMF theory.

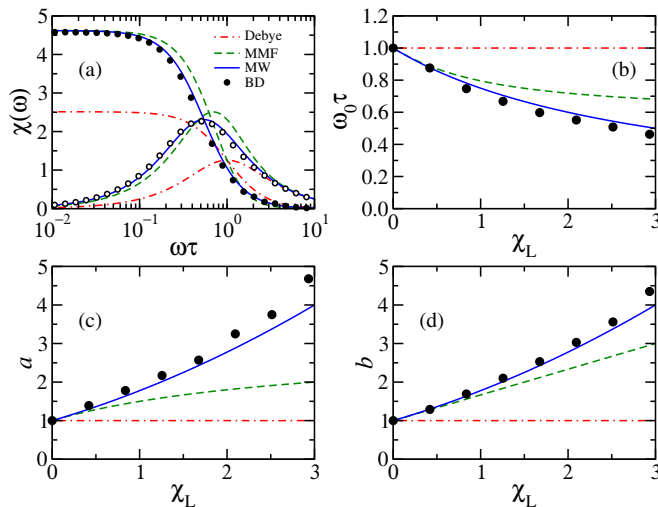


FIG. 1. Results for monodisperse ferrofluids with $\lambda = 1$: (a) $\chi(\omega)$ for a system with $\varphi = 0.314$; (b) ω_0 ; (c) a ; (d) b . The dot-dashed red lines are from Debye theory, the dashed green lines are from MMF theory, and the solid blue lines are from MW theory. The points are from BD simulations [15]. In (a), filled symbols are the real part, and open symbols are the imaginary part.

An essential feature of a ferrofluid is its polydispersity. New BD simulations were carried out on a bidisperse mixture of small particles with diameter $\sigma^{(s)}$, dipolar cou-

pling constant $\lambda^{(s)} = 1$, and Brownian rotational time $\tau^{(s)}$, and large particles with $\sigma^{(l)} = (4/3)\sigma^{(s)}$, $\lambda^{(l)} = 2$, and $\tau^{(l)} = (4/3)^3\tau^{(s)}$ (System A). The system parameters are given in Table I, and are typical values for real magnetite ferrofluids. The volume fraction of each component was chosen so that $\chi_L^{(s,l)} = 8\varphi^{(s,l)}\lambda^{(s,l)} = \frac{1}{2}\chi_L$ and $0.80 \leq \chi_L \leq 3.20$. The number fraction of small particles was $p^{(s)} = 0.826$.

TABLE I. Parameters for System A [$\lambda^{(s)} = 1$, $\lambda^{(l)} = 2$, $\sigma^{(l)}/\sigma^{(s)} = (4/3)$, $\tau^{(l)}/\tau^{(s)} = (4/3)^3$] and System B [$\lambda^{(s)} = 1$, $\lambda^{(l)} = 2$, $\sigma^{(l)}/\sigma^{(s)} = 1$, $\tau^{(l)}/\tau^{(s)} = 10$]. $\chi_L = \chi_L^{(s)} + \chi_L^{(l)}$ is the total Langevin susceptibility, $\chi_{\text{MMF}} = \chi_{\text{MW}}$ is the susceptibility from MMF and MW theories, and χ_{BD} is the susceptibility from BD simulations. In the simulations, System A contained 423 small particles and 89 large particles ($p^{(s)} = 0.826$), and System B contained 381 small particles and 131 large particles ($p^{(s)} = 0.744$).

System	A	A	A	A	B
$\varphi^{(s)}$	0.0500	0.1000	0.1501	0.2001	0.1814
$\chi_L^{(s)}$	0.4002	0.8004	1.2005	1.6007	1.4511
$\varphi^{(l)}$	0.0249	0.0499	0.0748	0.0998	0.0624
$\chi_L^{(l)}$	0.3992	0.7983	1.1975	1.5966	0.9979
χ_L	0.7993	1.5987	2.3980	3.1974	2.4489
$\chi_{\text{MMF}} = \chi_{\text{MW}}$	1.0123	2.4506	4.3148	6.6050	4.4480
χ_{BD}	1.030(4)	2.467(9)	4.34(2)	6.68(3)	4.50(3)

Figure 2 shows $\chi(\omega)$ for System A at four concentrations. Even with the lowest value of χ_L , the Debye theory is inadequate, while MMF and MW theories are almost indistinguishable. As χ_L is increased, MW theory describes the changing frequency dispersion accurately, even beyond the $\chi_L = 3$ threshold of Weiss theory, while MMF theory overestimates the peak frequency and peak height in $\chi''(\omega)$, and overestimates $\chi'(\omega)$ in the range $\omega\tau^{(s)} \simeq 0.1$ – 1 . At the highest concentration, particle interactions reduce the peak frequency by about 50%.

The phase lag in the magnetic response is given by $\Delta\phi(\omega) = \arctan[\chi''(\omega)/\chi'(\omega)]$. This is plotted in Fig. 3 for System A at four concentrations. With the lowest value of χ_L , the Debye theory deviates significantly from the BD simulation results, while MMF and MW theories work equally well. As χ_L is increased, MW theory tracks the BD results, while MMF theory develops significant deviations.

Figure 4 shows the dynamic response of System A as a Cole-Cole (parametric) plot of $\chi''(\omega)/\chi(0)$ against $\chi'(\omega)/\chi(0)$ [16]. Interestingly, the Debye theory is moderately accurate over the whole range of χ_L , while MMF theory shows increasing deviations with increasing χ_L . As before, MW theory is essentially perfect.

In all of the theories considered here, the input parameters are χ_L and τ for each component in the system. In Debye theory, $\chi(\omega)$ is linear in χ_L , while in MMF and MW theories, interactions give rise to nonlinear terms in χ_L . An interesting prediction arises for a bidisperse

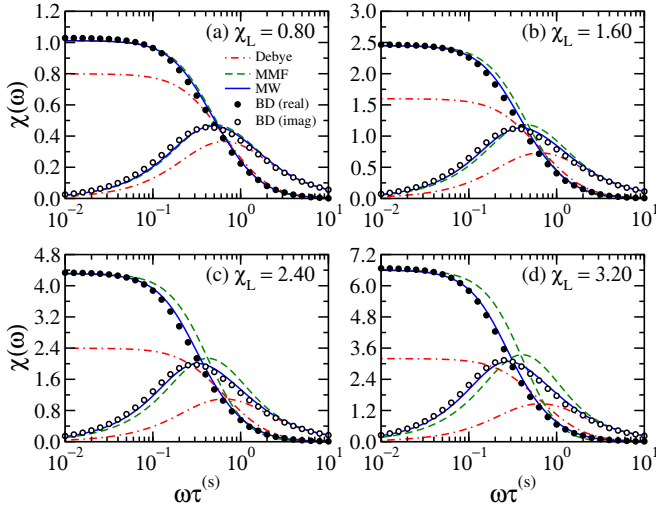


FIG. 2. $\chi(\omega)$ for a bidisperse ferrofluid (System A in Table I): (a) $\chi_L = 0.80$; (b) $\chi_L = 1.60$; (c) $\chi_L = 2.40$; (d) $\chi_L = 3.20$. The dot-dashed red lines are from Debye theory, the dashed green lines are from MMF theory, and the solid blue lines are from MW theory. The points are from BD simulations: filled symbols are the real part; open symbols are the imaginary part.

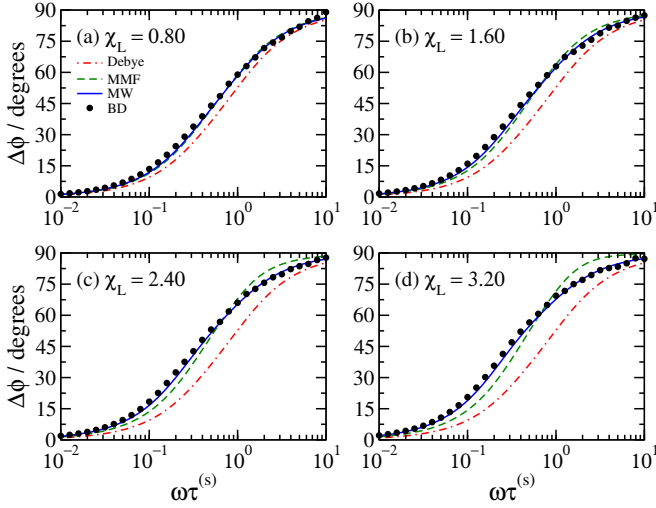


FIG. 3. $\Delta\phi$ for a bidisperse ferrofluid (System A in Table I): (a) $\chi_L = 0.80$; (b) $\chi_L = 1.60$; (c) $\chi_L = 2.40$; (d) $\chi_L = 3.20$. The dot-dashed red lines are from Debye theory, the dashed green lines are from MMF theory, and the solid blue lines are from MW theory. The points are from BD simulations.

system containing a large-particle component with a long rotational time $\tau^{(l)}$, and a small-particle component with a short rotational time $\tau^{(s)}$. In the Debye theory, the contributions from the two components are strictly additive. With interactions, the low-frequency susceptibility should show a strong enhancement because both the small-particle and large-particle components contribute, and there is coupling between them, while at high frequencies, the large particles are frozen out, and so only

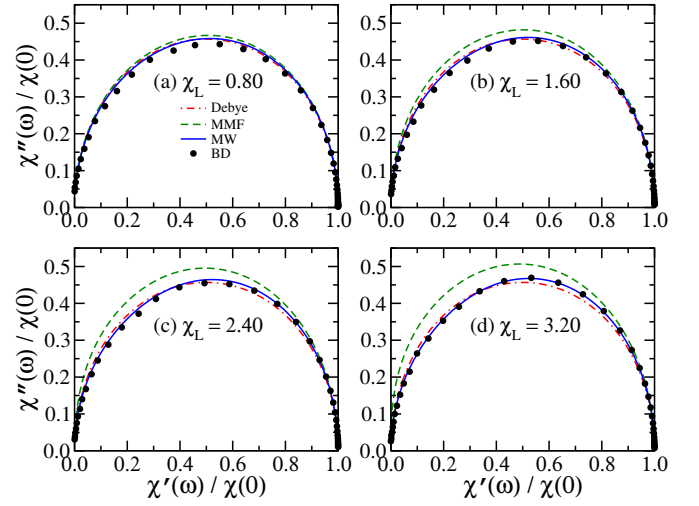


FIG. 4. Cole-Cole plot for a bidisperse ferrofluid (System A in Table I): (a) $\chi_L = 0.80$; (b) $\chi_L = 1.60$; (c) $\chi_L = 2.40$; (d) $\chi_L = 3.20$. The dot-dashed red lines are from Debye theory, the dashed green lines are from MMF theory, and the solid blue lines are from MW theory. The points are from BD simulations.

the small particles contribute. To illustrate this, results are presented for a bidisperse ferrofluid (System B) with parameters given in Table I. The essential features are that $\chi_L^{(s)} > \chi_L^{(l)}$ and $\tau^{(s)} < \tau^{(l)}$; for reasons explained below, the values were $\chi_L^{(s)} = 1.45$, $\chi_L^{(l)} = 1.00$, and $\tau^{(l)} = 10\tau^{(s)}$. The number fraction of small particles was $p^{(s)} = 0.744$.

Figure 5 shows all of the results for System B. $\chi'(\omega)$ and $\chi''(\omega)$ are shown in Fig. 5(a) and (b), respectively. The small-particle and large-particle contributions in the Debye theory are shown along with the total. For comparison, BD simulations were run for the noninteracting case by omitting the dipole-dipole interactions; the agreement between Debye theory and these simulations is perfect. Note that the high-frequency, small-particle peak in $\chi''(\omega)$ at $\omega\tau^{(s)} = 1$ is larger than the low-frequency, large-particle peak at $\omega\tau^{(s)} = 0.1$, because $\chi_L^{(s)} > \chi_L^{(l)}$. Results for the interacting case from MMF and MW theories, and new BD simulations, show much stronger enhancement at low frequency than at high frequency. This difference is so pronounced, that the low-frequency, large-particle peak in $\chi''(\omega)$ is now larger than the high-frequency, small-particle peak. The agreement between MW theory and BD simulations is essentially perfect, while MMF theory is only qualitatively correct. The phase lag is shown in Fig. 5(c). There are two separate steps with increasing frequency, corresponding to the large-particle and small-particle fractions. Results for the interacting case are described perfectly well by MW theory, MMF theory underestimates (overestimates) $\Delta\phi$ at low (high) frequency, and Debye theory is inaccurate. Finally, Fig. 5(d) shows the Cole-Cole plot. The BD simulation results for the noninteracting and interacting

cases are like mirror images of one another, and the system parameters were selected so that this was the case. Debye theory and MW theory are in perfect agreement with the simulation results for noninteracting and interacting systems, respectively, and MMF theory is somewhere in between. Interactions cause the low-frequency lobe to increase (all particles coupled) with respect to the high-frequency lobe (small particles coupled).

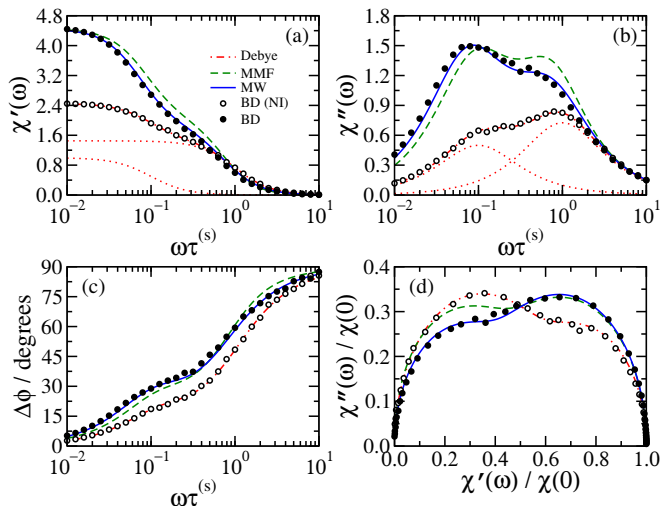


FIG. 5. Magnetic susceptibility spectrum for a bidisperse ferrofluid (System B in Table I): (a) real part; (b) imaginary part; (c) phase lag; (d) Cole-Cole plot. The dot-dashed red lines are from Debye theory, the dashed green lines are from MMF theory, and the solid blue lines are from MW theory. The points are from BD simulations: open symbols are for a noninteracting (NI) system; filled symbols are for an interacting system. In (a) and (b), dotted red lines show the individual small-particle (high-frequency) and large-particle (low-frequency) contributions to the Debye theory.

In this Rapid Communication, the dynamic magnetic response of a ferrofluid to a weak ac magnetic field was calculated theoretically including interparticle interac-

tions at various levels of approximation. The first conclusion is that the effects of interactions are very significant. With realistic parameters, the amplitude of the dynamic magnetic response was enhanced by up to 100%, and the frequency of maximum power loss was reduced by up to 50%, as compared to the noninteracting case. The second conclusion is that systematic improvements on the description of interparticle correlations yield successively accurate predictions for the dynamic magnetic susceptibility. As compared to BD simulations, MW theory was essentially perfect over the whole range of parameters tested, including in the region where Weiss theory fails. The third conclusion is that the effects of particle-size polydispersity are very pronounced. It was demonstrated that the qualitative appearance of the susceptibility spectra can be changed by including interparticle interactions between small-particle and large-particle components.

The accurate theory of the effects presented here can be used to characterize the particle-size distribution through fitting to a susceptibility spectrum, by analogy with a fit to a magnetization curve [5] or a sedimentation profile [17]. The general phenomena described herein are not limited to ferromagnetic particles undergoing Brownian rotation [1]; they will also occur with superparamagnetic nanoparticles undergoing Néel rotation, and with paramagnetic micron-sized particles in magnetorheological fluids, the essential features being that there are strong interparticle interactions, and a separation of re-orientational timescales. The theory outlined here can also be applied to magnetic polymers (ferrogels) [18], magnetic particles trapped in biological tissue [7], and many other areas of application.

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